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<b>(21) International Application Number:</b> PCT/US95/06162 <b>(22) International Filing Date:</b> 19 May 1995 (19.05.95)  <b>(30) Priority Data:</b> 08/268,319 30 June 1994 (30.06.94) US  <b>(71) Applicant:</b> MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint-Paul, MN 55133-3427 (US).  <b>(72) Inventor:</b> CROFT, Thomas, Stone; 6801 River Place Boulevard, Austin, TX 78726-9000 (US).  <b>(74) Agents:</b> NEAVEILL, Darla, P. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		<b>(81) Designated States:</b> CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> POLYURETHANE/UREA ELASTOMERIC SEALANTS  <b>(57) Abstract</b>  A polypropylene ether polyol based polyurethane elastomer comprising a polyisocyanate component, and an isocyanate reactive component comprising at least one polypropylene ether polyol containing from 5 to 60 percent dispersion selected from polyadduct and polycondensate dispersions, with from 1 to 35 percent of at least one epoxy compound, said elastomer having an isocyanate index up to 100.		

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POLYURETHANE/UREA ELASTOMERIC SEALANTSBackground of the InventionField of the Invention

5        This invention relates to fuel resistant polymeric elastomers and to articles formed therefrom useful as encapsulants, sealants, potting compounds, end seals, coatings and dams for electrical and telecommunication devices and as fuel resistant sealants for fuel  
10 containers in the transportation industry.

Description of the Related Art

Elastomers and sealants containing polyurethanes and polyurethane/ureas are well known in the art. It is also  
15 known that the polyols used in such polyurethanes provide elasticity and strongly influence the chemical resistance of the system. Polyols are thus selected dependent on the application for the elastomer.

For example, polypropylene ether polyols are  
20 typically used in applications where resistance to hydrolysis and low temperature flexibility is important, however they suffer from low resistance to swelling by hydrocarbons. Polyester polyols are used when hydrocarbon fuel resistance is important, but they are  
25 highly susceptible to hydrolytic attack. Protective ingredients must be added to polyester based polyurethanes to decrease their susceptibility to attack by water if they are to be used in any application which requires even a moderate hydrolytic stability. However,  
30 even this has not proved to be entirely satisfactory. See, e.g., discussed Journal of Coated Fabrics 20, 188 (1991) concerning the premature failure of fuel tanks utilizing polyester based polyurethanes.

The properties of low temperature flexibility and  
35 fuel resistance conflict as the structural features, such

as high polarity, which provide fuel resistance typically also lead to reduced flexibility at low temperatures.

Recently the automotive and aircraft industries have also concentrated on efforts to reduce the overall weight  
5 in such applications as automotive assembly of the wheel house, fire walls and trunks. This also lessens the desirability of addition of protective ingredients which tend to add to the overall weight of the elastomer.

For example, certain polyester polyols, in  
10 combination with cycloaliphatic polyisocyanates, an amine coupling agent, and a "cement component" containing an epoxy, can be used to prepare hydrocarbon-resistant polyurethanes as disclosed in U.S. Pat. Nos. 4,668,535 and 4,565,729. The isocyanate index was taught to range  
15 from 80 to 120, desirably from 90 to 95. It is specifically stated that unsuitable fuel resistance results from the use of too little isocyanate, i.e., an isocyanate index below 80.

U.S. Pat. Nos. 4,487,913 and 4,247,678 discloses the  
20 use of methylene bis(4-isocyanato cyclohexane) and mixed polyesters to achieve fuel resistance. Three component mixtures comprising polyester isocyanate prepolymers, amine or ketimine curing agents, and a "cement component" are used to line fuel tanks in U.S. Pat. Nos. 4,554,300;  
25 4,554,299 and 4,496,707. An epoxy compound was included in the "cement" component. Again, it is taught that compositions having an isocyanate index below 80 exhibit unsuitable fuel resistance and/or hydrolysis resistance.

Fuel resistant translucent pasty sealants are  
30 obtained in U.S. Pat. No. 3,158,586 from polyester and polyether isocyanate prepolymers, aromatic amine crosslinkers, and liquid diglycidyl ethers. The active hydrogen materials are described as being present in about equal amounts to the available isocyanate groups.

U.S. Pat. No. 5,001,167 discloses a polyurethane polymer based on a polyether polyol containing at least 50 weight percent oxyethylene units which is suitable for hydrocarbon environments. However, it is taught that the polymer is preferably used in environments with little water exposure. Water causes swelling of the polymer due to the high oxyethylene content in the polyol segment. It is further taught that polymer dispersions in polyols should be avoided due to the undesirable hardness of elastomers including such dispersions.

The preparation of epoxy (epoxy hardener) polymer dispersions in polyols are disclosed in U.S. Pat. No. 4,789,690 for use in polyurethane foams and in U.S. Pat. No. 4,305,861 as clouding agents for plastic materials. Polyurethane foams and elastomers are derived from linear and branched polyols and polyisocyanates at an isocyanate index of from about 65 to about 85 as taught in U.S. Pat. No. 4,722,946. It is specifically stated that isocyanate indices below 65 do not give a product with useful consistency. It is also taught in this reference that elastomers disclosed in U.S. Pat. No. 4,476,258 having an isocyanate index below 65 could not be duplicated, but attempts instead provided liquid materials, which are not useful for the purpose intended. U.S. Pat. No. 4,476,258 had discussed elastomers from urethane forming components in less than stoichiometric amounts.

It would be extremely desirable to prepare polyurethanes exhibiting resistance to hydrocarbons from relatively inexpensive polypropylene ether based polyols. The use of propylene ether polyols in polyurethanes would yield elastomers exhibiting more resistance to hydrolysis than those based on polyester polyols, while providing good low-temperature properties.

It has now been discovered that fuel resistant polypropylene oxide based polyurethanes can be produced from an unexpected synergism of polypropylene ether polyols containing polyadduct and polycondensate  
5 dispersions and epoxy compounds. Propylene oxide based polyurethanes disclosed herein exhibit a surprising correlation between the weight percent change in kerosene and the total weight percent in the composition of organic polyadduct and/or polycondensate dispersion  
10 particles and epoxy compounds (based on the total polyurethane formulation). The percent weight gain when soaked in kerosene is reduced from over 50 percent by weight to less than 10 percent.

It has now also been discovered that useful fuel  
15 resistant viscoelastic elastomers can be obtained even at extremely low isocyanate indices, e.g., even to 10 or below. The resulting materials have excellent fuel resistance and hydrolytic stability combined with excellent low temperature flexibility. By the proper  
20 balancing of the nature and reactivity of the isocyanate reactive compounds and the polypropylene ether polyols containing a combination of polyadducts and polycondensate dispersions and epoxy compounds, elastomers may be prepared having viscoelastic  
25 characteristics ranging from firm elastomers to jelly-like sealants, as desired for varying applications.

The sealants of the present invention are particularly useful for cable splice closures that provide a protective barrier for sealing splice cases or  
30 closures for wires or wire pairs or fiber optic fibers or other outside telecommunication apparatus from damage caused by environmental exposure. Historically, such sealants have been based on butyl rubber and do not perform well in hydrocarbon contaminated environments  
35 commonly found in manholes.

Soft gel-like sealants of the present invention can be used to fill connecting devices for telecommunication or electrical or automotive applications for providing fuel and water resistant electrical or signal connections.

#### Summary of the Invention

The invention provides kerosene resistant polypropylene ether polyol based polyurethane elastomers and polypropylene ether polyol based polyurethane/urea elastomers having isocyanate equivalent indices of up to 100, preferably up to 80. The isocyanate indices may be extremely low e.g., even to 10 or below.

Specifically, the invention comprises a polypropylene ether polyol based polyurethane elastomer comprising

- a) a polyisocyanate component,
- b) an isocyanate reactive component comprising at least one polypropylene ether polyol containing from 5 to 60 percent dispersion selected from polyadduct and polycondensate dispersions,

said dispersion further comprising from 1 to 35 percent of at least one epoxy compound, said elastomer having an isocyanate index of up to 100, wherein the total amount of the dispersion and the epoxy comprises from 5 to 45 percent of the composition,

wherein said a tensile dumbbell formed from said elastomer exhibits a weight gain of less than 20% after being immersed in kerosene for 24 hours at 38°C.

Preferred polypropylene ether polyol based polyurethane elastomers of the invention comprise:

- a) from 1 to 50 percent of a polyisocyanate component,

- b) at least 20 percent of at least one isocyanate reactive component comprising at least one polypropylene ether polyol containing 15 to 40 percent of a dispersion selected from polyadduct and polycondensate dispersions,
- 5 c) and from 5 to 35 percent of at least one epoxy compound, said elastomer having an isocyanate index of up to 100,

said elastomer exhibiting less than a 10 percent weight gain when a tensile dumbbell is immersed in kerosene for 10 24 hours at 38°C.

The resulting materials have excellent kerosene resistance, with the preferred materials exhibiting less than twenty percent, most preferably less than ten 15 percent, when a Die C (ASTM D412) tensile dumbbell is immersed in kerosene for 24 hours at 100°F (38°C). Highly preferred materials exhibit less than five percent weight gain when a Die C (ASTM D412) tensile dumbbell immersed in kerosene for 24 hours at 100°F (38°C).

20 Excellent hydrolytic stability was also observed with the preferred materials exhibiting less than a five percent weight gain after seven days in boiling water, 212°F (100°C) for 2.5 by 5 by 1.3 cm specimens.

Elastomeric materials based on the invention 25 generally have excellent low temperature flexibility with a glass transition temperature (Tg) typically below -46°C (-50°F).

The incorporation of a polyester polyol or polycarbonate polyol to the predominantly polypropylene 30 ether polyol can further improve the kerosene resistance. Suitable polyols and polyamines have molecular weights of 100 to about 100,000, preferably from 400 to 20,000, most preferably from 800 to 20,000.



Useful polyamines may have primary or secondary amine groups.

In another embodiment, an elastomer of the invention comprises hollow microspheres as a filler, preferably  
5 from 10 to 60 volume percent.

The invention also provides encapsulants, potting compounds, sealants, endseals, coatings, vibration damping devices and the like comprising elastomers of the invention.

10 As used herein, these terms have the following meanings.

1. The term "elastomer" refers to a rubbery material which, when deformed, will return to approximately the original dimensions in a relatively  
15 short time.

2. The term "isocyanate index" and "NCO-index" as used herein refer to the ratio of NCO groups over reactive hydrogen atoms present in a polyurethane formulation given as a percentage:

20 
$$\text{NCO-Index} = \frac{(\text{NCO})}{(\text{active hydrogen})} \times 100$$

In other words, the NCO- index expresses the percentage  
25 of isocyanate actually used in a formulation with respect to the amount of isocyanate theoretically required for reacting with the amount of isocyanate reactive hydrogen used in a formulation.

The expression "active hydrogen atoms" as used here  
30 for the purpose of calculating the isocyanate index refers to the total of hydroxyl and amine hydrogen atoms present in the reactive compositions in the form of polyols and polyamines. This means that for the purpose of calculating the isocyanate index one hydroxyl group is  
35 considered to comprise one active hydrogen and one primary amine group is considered to comprise two active hydrogens. The Zerewitnoff test used to determine active

hydrogen is described in Journal of the American Chemical Society, Volume 49, page 3181 (1927).

3. The term "isocyanate reactive material" means a compound or blend of compounds containing active hydrogen  
5 atoms.

4. The terms "equivalent weight" and "molecular weight" as used throughout the present specification refer to equivalent weight values that may be calculated by measuring the content of functional groups per weight  
10 of sample, and the molecular weight values that may be calculated from the aforementioned equivalent weight and the theoretical functionality of the compound (i.e., by the total number of hydrogen atoms attached to an oxygen atom and/or a nitrogen atom).

5. The term "polyol" means a substance containing at least two hydroxyl groups attached to a single  
15 molecule.

6. The term "polyamine" means a substance containing at least two primary or secondary amino groups  
20 attached to a single molecule.

7. The term "essentially inert" as used herein means that the plasticizer does not become cross-linked into the polyurethane/polyurea reaction product.

8. The term "non-exuding" as used herein means  
25 that the plasticizer has the ability to become and remain blended with the polyurethane/polyurea reaction product. Many excellent plasticizers experience some blooming, or a slight separation from the solid, especially at higher temperatures, and over lengthy storage times. These  
30 plasticizers are still considered to be "substantially non-exuding."

9. The term "polymer polyol" or "polymer polyol composition" as employed throughout the specification and appended claims, means a liquid or low-melting polyol,  
35 polyol containing blend or polyol blend containing

polyadducts and polycondensates in a finely dispersed or dissolved form, e.g., a dispersion polymer polyol, a grafted copolymer polyol, a solution polymer polyol or blends thereof.

5        10. The term "total unsaturation level" refers to the total unsaturation levels as determined by procedure ASTM D 2849-69 or equivalent procedure.

10        11. The term "predominantly polypropylene ether polyol" means a polymer of propylene oxide or mixtures of propylene oxide and ethylene oxide, in which the oxypropylene units derived from the propylene oxide constitute at least 50%.

12. The term "polyurethane elastomer" includes polyurethane and polyurethane\urea elastomers.

15        13. The term " $T_g$ " means glass-rubber transition temperature.

14. The term "vibration-damping material" means a material which undergoes shear deformation in the presence of vibration forces and dissipates some of its inelastic deformation energy as heat.

20        15. The term "tan delta" is a damping term which is a measure of a ratio of the energy dissipated as heat (loss modulus  $G''$ ) to maximum energy stored elastically (Storage modulus  $G'$ ) during one cycle of oscillation. (Tan delta =  $G''/G'$ ).

25        Percents, ratios and parts described herein are by weight unless otherwise specifically stated.

#### Description of the Drawings

30        Figure 1 indicates that the percent weight gain in kerosene can be reduced to less than 10 percent when the total weight percent of organic polyadducts and/or polycondensate dispersion particles and epoxy compounds (based on the total polyurethane formulation) approaches 35 40 percent. It should be appreciated that this critical

value will decrease when a polyester polyol or polycarbonate polyol or the like is included in the polyurethane formulation.

5                   Detailed Description of the Invention

Polyisocyanates

Useful elastomers of the invention comprise at least one isocyanate component. Suitable isocyanate components include any isocyanate having the required functionality.

10           The isocyanate component is present in sufficient amount to provide an isocyanate index of below 150, more preferably below 100. Equivalents for each component can be calculated by dividing the actual weight (in parts) of each component by the equivalent weight.

15           The term isocyanate also includes isocyanate-terminated prepolymers. Polyisocyanates may be linear or branched, aliphatic, cycloaliphatic, araliphatic, heterocyclic or aromatic, or any combination of such polyisocyanates.

20           Particularly suitable polyisocyanates correspond to the formula



wherein n is an integer of from 2 to 4, and Q is selected from aliphatic hydrocarbon radicals containing from 2 to  
25 100 carbon atoms, and zero to 50 heteroatoms;  
cycloaliphatic hydrocarbon radicals containing from 4 to 100 carbon atoms and zero to 50 heteroatoms; aromatic hydrocarbon radicals or heterocyclic aromatic radicals containing from 6 to 15 carbon atoms and zero to 10  
30 heteroatoms, and araliphatic hydrocarbon radicals containing from 8 to 100 carbon atoms and zero to 50 heteroatoms.

Useful heteroatoms in Q include non-peroxidic oxygen, sulfur, non-amino nitrogen, halogen, silicon, and  
35 non-phosphino phosphorus.

Examples of polyisocyanates include ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, 1,12-dodecane diisocyanate, cyclobutane-  
5 1,3-diisocyanate, cyclohexane-1,3 and 1,4-diisocyanate and mixtures thereof, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (German Auslegeschrift No. 1,202,785, U.S. Pat. No. 3,401,190), 2,4- and 2,6-hexahydrotolylene diisocyanate and mixtures thereof,  
10 hexahydro-1,3 and/or -1,4- phenylene diisocyanate, hexahydro-2,4'- and/or 4,4'-diphenylmethane diisocyanate, 1,3-and 1,4-phenylene diisocyanate, 2,4- and 2,6-tolylene diisocyanate and mixtures thereof, diphenylmethane-2,4'- and/or 4,4'-diisocyanate, naphthylene-1,5-diisocyanate,  
15 C<sub>36</sub> dimer acid diisocyanate (DDI) and the reaction products of four equivalents of the aforementioned isocyanate-containing compounds with compounds containing two isocyanate-reactive groups.

Also useful are e.g., triphenyl methane-4,4', 4"-  
20 triisocyanate, polyphenyl polymethylene polyisocyanates of the type obtained by condensing aniline with formaldehyde, followed by phosgenation, (British Pat. Nos. 874,430 and 848,671), m- and p-isocyanatophenyl sulphonyl isocyanates (U.S. Pat. No. 3,454,606),  
25 perchlorinated aryl polyisocyanates (U.S. Pat. No. 3,277,138), polyisocyanates containing carbodiimide groups (U.S. Pat. Nos. 3,152,162, 4,088,665 and 4,344,855), norbornane diisocyanates (U.S. Pat. No. 3,492,330), polyisocyanates containing allophanate groups  
30 (British Pat. No. 994,890, Belgian Pat. No. 761,626 and U.S. Pat. No. 3,769,318), polyisocyanates containing isocyanurate groups (U.S. Pat. Nos. 3,001,973, and 3,738,957, German Pat. Nos. 1,022,789, 1,222,067 and 1,027,394, and German Offenlegungsschrift No. 1,929,034),  
35 polyisocyanates containing urethane groups (Belgian Pat.

No. 752,261 and U.S. Pat. 3,394,164 and 3,644,457), polyisocyanates containing acrylated urea groups (U.S. Patent No. 3,517,039), polyisocyanates containing biuret groups (U.S. Pat. Nos. 3,124,605, and 3,201,372 and  
5 British Pat. No. 889,050), polyisocyanates produced by telomerization reactions (U.S. Pat. No. 3,654,106), polyisocyanates containing ester groups (British Pat. Nos. 964,474 and 1,072,956, U.S. Pat. No. 3,567,763 and German Pat. No. 1,231,688), reaction products of the  
10 above-mentioned diisocyanates with acetals (German Patent No. 1,072,385), polyisocyanates containing polymeric fatty acid esters (U.S. Patent No. 3,455,883), and araliphatic polyisocyanates (U.S. Patent No. 4,051,166).

Also useful are distillation residues having  
15 isocyanate groups obtained in the commercial production of isocyanates, optionally in solution in one or more of the above-mentioned polyisocyanates. It is also possible to use mixtures of any of the above-mentioned polyisocyanates.

20 Preferred polyisocyanates include hexamethylene diisocyanate, the isocyanurate and the biuret thereof; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (isophorone diisocyanate); the tolylene diisocyanates and isocyanurates thereof; the mixed isocyanurate of tolylene  
25 diisocyanate and hexamethylene diisocyanate; the reaction product of 1 mol of trimethylol propane and 3 mols of tolylene diisocyanate, diphenyl methane diisocyanate, dimer acid diisocyanate (DDI) and 4,4'-methylene-bis (cyclohexyl diisocyanate).

30 Certain blocked isocyanates are also useful in compositions of the invention. Blocking of polyisocyanates with phenols, acetoacetic ester, diethyl malonate, butanone oxime, epsilon caprolactam and the like is a well-known procedure for the temporary

retardation of reactions between polyisocyanates and active hydrogen containing compounds.

The starting polyisocyanates used for the preparation of the blocked polyisocyanates include  
5 organic polyisocyanates having an average molecular weight of 200 to 25,000 which include derivatives of monomeric organic polyisocyanates, in particular derivatives containing biuret, isocyanurate and/or urethane groups. The derivatives are preferably  
10 isocyanate group-containing prepolymers which can be obtained, for example, by the reaction of relatively high molecular weight polyhydroxyl compounds with di- or polyisocyanates.

Suitable starting compounds for the preparation of  
15 such prepolymers include low molecular weight polyether or polyester polyols. Preferred starting materials are the polyhydroxyl compounds having a molecular weight of 300 to 20,000, preferably 1000 to 5000.

Examples of these relatively high molecular weight  
20 polyhydroxyl compounds include the polyester polyols, polylactones, polyether polyols, amine or amide based polyether polyols, polycarbonates containing hydroxyl groups, polythioether polyols, and polyacetals described later. Particularly suitable are polypropylene oxide  
25 glycol and the polypropylene oxide adduct of trimethylol propane. Examples of polyisocyanates suitable for blocking include isophorone diisocyanate, toluene diisocyanate, hexamethylene diisocyanate, and diphenyl methane diisocyanate. Aromatic polyisocyanates are,  
30 however, preferred due to the lower unblocking temperature. The blocking agents are reacted in well known procedures with the polyisocyanate prepolymer to form a blocked polyisocyanate prepolymer. Depending on the structure of the blocked polyisocyanates, the  
35 polyisocyanate can be regenerated at a temperature above

100°C for further reaction to form the polyurethane/polyurea elastomers of the present invention. Illustrative of these materials are 4-nonylphenol blocked isocyanate prepolymers available as  
5 Desmocap™ from Miles.

#### Epoxy Compound

Elastomers of the invention also comprise from 1 to 35 percent, preferably from 5 to 30 percent, by weight of  
10 an epoxy compound.

The epoxy compound contains one or more epoxide groups per molecule. It may be monomeric or polymeric, saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted with  
15 other substituents such as hydroxyl groups, ether radicals, halogen atoms and the like. The epoxy groups may be terminal or inner 1,2-epoxy groups and may be linked to an oxygen atom, i.e., glycidyl ether or glycidyl ester groups.

20 Compositions of the invention preferably have an epoxide equivalent weight from 90 to 950, preferably from 170 to 450 and most preferably from 170 to 220. The average epoxy equivalent weight is figured by dividing the average molecular weight of the resin by the number  
25 of epoxy groups per molecule.

Epoxy compounds having low epoxide equivalents, in the range of 90 to 250, are typically preferred because of their lower viscosity, although higher equivalent weight compounds, including those up to 950, with melting  
30 points up to 75°C, offer advantages where viscosity is not a factor. Liquid epoxy compounds, of from 170 to 220, are most preferred.

Suitable examples include epoxy compounds from the reaction of polyphenols and epihalohydrins, polyalcohols  
35 and epihalohydrins, polycarboxylic acids and



epihalohydrins, amines and epihalohydrins, sulfur containing compounds and epihalohydrins, mixtures of the above compounds and epihalohydrin, polyisocyanates and 2,3-epoxy-1-propanol and from epoxidation of olefinically unsaturated compounds.

Preferred epoxies include the products of reactions of epihalohydrin and aromatic polyhydro-phenolic compounds, including glycidyl ethers of bisphenol A compounds, or phenolic resins such as a phenol-formaldehyde resin. Preferred types of these resins are bisphenol A type epoxy resins having average epoxy equivalent weights of from 170 to 220, brominated bisphenol A type epoxy resins which have average epoxy equivalent weights of from 300 to 800.

Suitable examples include polyglycidyl ethers of polyhydric phenols, for example, bis(4-hydroxyphenyl) methane, 2,2-bis(4-hydroxyphenyl)propane, bis(4-hydroxylphenyl)sulfone, tris(4-hydroxylphenyl)methane and 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane and the like, and reaction products, of monovalent or higher valent phenols with aldehydes, in particular, formaldehyde, commonly called Novolak resins. Commercially available resins from bisphenol A and epihalohydrin include Epon™ 826 from Shell Chemical Company. A typical Novolak resin is "D.E.N. 431" from the Dow Chemical Company.

Other suitable polyepoxides include but are not limited to glycidyl ethers of aromatic amines, such as N,N,N',N'-tetraglycidyl methylene dianiline; glycidyl esters of polyvalent aromatic, aliphatic and cycloaliphatic acids, such as diglycidyl phthalate and hexahydrophthalic acid diglycidyl ester; glycidyl ethers of polyhydric alcohols, such as the diglycidyl ether of hydrogenated bisphenol A; epoxidation products of polyunsaturated compounds such as certain vegetable oils;

epoxidized polymers such as epoxidized butadiene-acrylonitrile copolymer; epoxides of cycloaliphatic esters of dicarboxylic acids, such as bis(3,4-epoxycyclohexyl methyl)-adipate; epoxides of  
5 cycloaliphatic esters, such as 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, and the like; hydantoin epoxy resins; and glycidyl ethers of polypropylene ether glycols, such as "D.E.R. 736" available from Dow Chemical Company.

10 Numerous additional suitable polyepoxide materials are commercially available or readily prepared using well known techniques and these will be apparent to those skilled in the art.

The amount of the epoxy compound typically ranges  
15 from 1 to 35 parts, preferably from 5 to 30 parts, based on the total formulation.

The epoxy compound can be incorporated as unreacted or partially reacted epoxy compounds in an epoxy resin polymer polyol dispersion.

20

#### Isocyanate Reactive Component

The materials of this invention also contain an isocyanate reactive component containing at least one polypropylene ether polyol containing a polyadduct or a  
25 polycondensate dispersion. The total isocyanate reactive component is present at greater than 20 percent, preferably greater than 30 percent, by weight of the total elastomeric product.

Suitable polypropylene ether polyols contain from 5  
30 to 60 percent, preferably 15 to 40 percent, polymer dispersions in polyols. Mixtures of suitable polymer polyols may be employed. At least one predominantly polypropylene ether polyol containing polyadducts or polycondensates is necessary for the practice of this  
35 invention.

Useful predominantly polypropylene ether polyols, are polymers of propylene oxide or mixtures of propylene oxide and ethylene oxide, in which the oxypropylene units derived from the propylene oxide constitute at least 50%,  
5 more preferably at least 65%, most preferably at least 75% by weight of the polyether. In addition, the polypropylene oxide polyols should have a total unsaturation content of less than 0.08, preferably less than 0.06, more preferably less than 0.04 and most  
10 preferably less than 0.02 milliequivalents/gram polyol.

Suitable polypropylene ether polyols are polyhydroxyl compounds which contain high molecular weight polyadducts and polycondensates in a finely dispersed or dissolved form, e.g., a dispersion polymer  
15 polyol, a grafted copolymer polyol, a solution polymer polyol, or blends thereof. Polyhydroxyl compounds such as these are obtained, e.g., by carrying out polyaddition reactions and polycondensation reactions in situ in polyols.

20 Thus, polyisocyanates may be reacted with themselves (trimerized) to form polyisocyanurate dispersions as disclosed in U.S. Pat. Nos. 4,386,167 and 4,359,541; with hydrazine to form polyhydrazo-dicarbonamide dispersions as taught in U.S. Pat. Nos. 4,042,537; 4,093,569 and  
25 5,068,280; with alkanolamines to form polyurethane urea dispersions as disclosed in U.S. Pat. Nos. 4,293,470, 4,296,213, 4,374,209 and 4,452,923; with primary hydroxyl short chain polyols to form polyurethane dispersions as taught in U.S. Pat. Nos. 4,438,252 and 4,497,913; or with  
30 aminoplast or phenoplast as disclosed in U.S. Pat. No. 4,260,530, and reaction of an oxalate ester and a diamine to form polyoxanate polymer polyol dispersions as taught in U.S. Pat. No. 4,407,983.

Polyhydroxyl compounds can also be modified by vinyl  
35 polymers of the type obtained, for example, by

- polymerizing styrene and acrylonitrile in the presence of polyethers (U.S. Pat. Nos. 3,304,273; 3,383,351; 3,652,639; and 5,093,412). Plastics having particularly good flameproof properties are obtained by using
- 5 polyether polyols modified (German Offenlegungsschrift Nos. 2,644,922 and 2,646,141 and U.S. Pat. No. 4,028,434) by graft polymerization with vinyl phosphonic acid esters and, optionally (meth)acrylonitrile, (meth)acrylamide or hydroxyl functional (meth)acrylic acid esters.
- 10 Polyhydroxyl compounds into which carboxyl groups have been introduced by radical graft polymerization with unsaturated carboxylic acids and other olefinically unsaturated monomers (U.S. Pat. Nos. 4,250,077 and 4,207,227) may be used in combination with mineral
- 15 fillers.

Also suitable are melamine, urea or urea/melamine blend particles dispersed in a polyol (U.S. Pat. Nos. 5,087,384; 5,106,883 and 5,153,233). Regardless of the specific polyol used, it is generally preferred to use

20 polyols containing primary hydroxy groups. Mixtures of polymer dispersions and conventional polyols may be employed.

Commercially available examples of predominantly polypropylene ether polyols include Multranol™ 9151 and

25 9238, available from Miles Chemical Corporation; Arcol™ 34-28, available from Arco Corporation, and Pluracol™ 994, available from BASF Agtiengesellschaft.

Also suitable as "polymer polyols" are epoxy resin dispersions prepared by reacting an epoxy compound with

30 an epoxy reactive curing agent in the presence of a liquid polyol. Suitable polymer polyol dispersion result from reacting epoxy compounds with epoxy curing agents such as amines, hydrazine, hydrazide or ammonia as described in U.S. Pat. No. 4,305,861.

Typically, the epoxy compound and epoxy curing agent are dissolved in the polyols and the polyaddition reaction to form the dispersed polymer particles carried out over a period between 30 minutes and 10 days, preferably between 6 hours and 72 hours, at a temperature of 0°C to 150°C with 50°C to 70°C working well. During this process, the initially clear solution changes into a milky dispersion containing from 5 to 60 percent by weight, preferably 5 to 40 percent by weight, most preferably 15 to 30 percent polymer particles, based on the total weight of the polymer polyol dispersion. Reaction times are a function of the temperature and are dependent upon the chemical structure of the epoxy resins and the epoxy curing agents.

15 The various epoxy compounds described supra are also useful to form epoxy resin "polymer polyol" dispersions.

The epoxy compound should have an average of at least 1.5, generally at least 2, reactive 1,2-epoxy groups per molecule, with an average of up to six, preferably up to four, most preferably up to 3, reactive 1,2-epoxy groups per molecule. Preferred epoxy compounds are directly soluble in the polyols but the epoxy compound may be dissolved in inert solvents or solubilizing agents such as low viscosity monoepoxides which may participate in the curing reaction if not soluble in the polyol.

25 A variety of known epoxy curing agents may be used to prepare the polyol dispersion, including those which have 2 or more amine groups. Difunctional to hexafunctional primary amines, amides, hydrazides and hydrazine are preferred, more preferably di- to tetrafunctional. Aliphatic, cycloaliphatic and/or aromatic diamines, are especially preferred, particularly di-primary amines with average molecular weights of 30 to 600, preferably 60 to 400.

Examples include alkylene polyamines such as 1,3-diaminopropane, 1,6-hexamethylene diamine, ethylenediamine, 1,10-decamethylene diamine, diethylene triamine, triethylenetriamine, tetramethylene pentamine; 5 cycloaliphatic diamines such as 1,4-, 1,3-, and 1,2-diaminocyclohexane, 4,4'-, 2,4'-, 2,2'-diamino dicyclohexylmethane, 3-aminomethyl-3,5,5-trimethylcyclohexylamine, 1,4-, and 1,3-diaminomethylcyclohexane; aromatic diamines such as meta- 10 xylene diamine; and other amine curing agents, such as ethanolamine, methylimino-bis(propyl)amine, aminoethylpiperazine, and polyoxypropylene diamines or triamines, and mixtures thereof. Again, it is preferred that the epoxy curing agents be soluble in the polyols but, if 15 not, it may be first dissolved in an inert solvent or a solubilizing agent.

Generally 0.4 to 5 moles of the epoxy compound are used per mole of the epoxy reactive curing agent. Preferably the mole ratio of the epoxy compound and the 20 epoxy reactive curing agent will be one or above to insure that any residual epoxy curing agent does not interfere in the polyurethane forming reaction. In such cases, the epoxy resin polymer polyol dispersion may contain unreacted or partially reacted epoxy compounds 25 and as such can act as both of the essential components of this invention, i.e., the polymer polyol and the epoxy compound.

For simplicity, the solids content is calculated as the sum of the weight of the epoxy compound and the epoxy 30 reactive curing agent divided by the weight of the total reaction mixture. However, the total weight percent of the organic polyadduct and/or polycondensate dispersion particles and epoxy compound added in addition to that used to prepare the epoxy resin must be above a critical

value (based on the total polyurethane formulation) to obtain the desired kerosene resistance.

Liquid polyols suitable as the dispersing medium, have functionalities of from 2 to 8, preferably from 2 to 4. "Liquid" means that the polyols are liquid at the temperature of the reaction of the epoxy resin and the epoxy reactive curing agent. Preferably used are polyester polyols, including ricinoleic acid derivatives, such as castor oil, polyoxyalkylene polyether polyols, and most preferably largely polypropylene ether polyols.

#### Additional Polyols or Polyamines

At least one member of the isocyanate reactive component must be a predominantly polypropylene ether polyol, however, additional polyols may also be present, i.e., the isocyanate reactive component may contain a blend of polyols. Polyols useful in such blends are liquid or quasi-liquid polyols, with functionality from 2 to 8, di- or trifunctional polyols being preferred. Suitable polyols have molecular weights of 400 to about 50,000, preferably 800 to 20,000.

Additional polyols may be selected from polyether polyols based on ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, epichlorohydrin or mixtures thereof, ricinoleic acid derivatives, e.g., castor oil; polyester polyols, polyamide or polyesteramide polyols; tertiary amine containing polyols, e.g., ethoxylated or propoxylated amides or amines; polyalkadiene polyols derived from butadiene polymers or copolymers, and hydrogenated derivatives thereof; polyacetals, polycarbonates containing hydroxyl groups; polyhydroxyl (meth)acrylic resins, polythioether polyols, polymer polyols, and the like.

Suitable classes of polyols include:

- (a) Polyethers containing at least 2, generally 2 to 8, preferably 2 or 3 hydroxyl groups obtained, for example, by polymerizing cyclic ethers, such as ethylene oxide, propylene oxide, hexane oxide, butylene oxide, tetrahydrofuran, styrene oxide or epichlorohydrin on their own, for example, in the presence of catalysts, such as double metal cyanide complexes or boron trifluoride, or by the addition of the epoxides, preferably ethylene oxide and propylene oxide, optionally in admixture or successively, with starter components containing reactive hydrogen atoms, such as water, alcohols, ammonia or amines, for example, ethylene glycol, 1,3-propylene glycol or 1,2-propylene glycol, trimethylol propane, glycerol, sorbitol, 4,4'-dihydroxy diphenyl propane aniline, ethanolamine or ethylene diamine. Sucrose polyethers (German Auslegeschrift Nos. 1,176,358 and 1,064,938) and formitol-or formose-started polyethers (U.S. Patent Nos. 4,187,355 and 4,247,654) may also be used.

The general term polyether polyols also includes polymers referred to as amine-based or amide-based polyols. When propylene oxide and ethylene oxide are utilized to prepare the polyether polyol, it is preferred that the oxypropylene content thereof be at least 50 weight percent, more preferably at least 65 weight percent and most preferably at least 75 weight percent. An especially preferred class of polyether polyol is a homopolymer of propylene oxide which is end-capped with up to 25 weight percent, based on the weight of the polyether, of oxyethylene units. Another especially preferred class of polyether polyol is a random copolymer of propylene oxide and up to 25 weight percent ethylene oxide, which may or may not additionally contain an end-cap of oxyethylene units. In addition, the polypropylene



oxide polyols should have a total unsaturation content of less than 0.08, preferably less than 0.06, more preferably less than 0.04 and most preferably less than 0.02 milliequivalents/gram polyol. The polyalkylene  
5 polyether polyols may have either primary or secondary hydroxyl groups in order to achieve the desired balancing of the nature and reactivity of the isocyanate reactive system in accordance with the present invention. However, in many cases, it is preferred to use at least  
10 one polyether polyol which predominately contains primary hydroxyl groups. Illustrative examples are the polypropylene oxide glycols, polypropylene oxide triols or ethylene oxide capped polypropylene oxide triols available either under the Arcol or Poly-L- trade names.  
15 (b) Esters of ricinoleic acid with polyhydric alcohols containing at least 2 hydroxyl groups, including mono, di-, and polyesters of ricinoleic acid. These ricinoleic acid polyol esters can be made by methods well known in the art, e.g., by direct esterification of  
20 ricinoleic acid with alcohols. A naturally occurring triglyceride of ricinoleic acid is castor oil which has an average functionality of 2.7. Suitable interesterification products may also be prepared from castor oil and substantially non-hydroxyl-containing,  
25 naturally occurring triglyceride oils (U.S. Pat. No. 4,603,188). Illustrative of the above materials is castor oil available from United Catalysts.

(c) Polyalkadiene polyols, prepared from dienes which include unsubstituted, 2-substituted or 2,3-  
30 disubstituted 1,3-dienes of up to 12 carbon atoms. Preferably, the diene has up to 12 carbon atoms. More preferably, the diene has up to 6 carbon atoms and the substituents in the 2-and/or 3-position may be hydrogen, alkyl groups having 1 to 4 carbon atoms, substituted  
35 aryl, unsubstituted aryl, halogen and the like. Typical

of such dienes are 1,3-butadiene, isoprene, chloroprene, 2-cyano-1,3-butadiene, 2,3-dimethyl-1,2-butadiene, and the like. Hydrogenated derivatives of the polyalkadiene polyols may also be used. A hydroxyl terminated  
5 polybutadiene is available from ARCO Chemicals under the designation "Poly-bd R-45HT".

(d) Polyesters containing hydroxyl groups, e.g., reaction products of polyhydric, preferably dihydric and, optionally, trihydric alcohols with poly-basic,  
10 preferably dibasic, carboxylic acid. Instead of using the free polycarboxylic acids, it is also possible to use the corresponding polycarboxylic acid anhydrides or corresponding polycarboxylic acid esters of lower alcohols or mixtures thereof for producing the  
15 polyesters. The polycarboxylic acids may be saturated or unsaturated aliphatic or cycloaliphatic, aromatic and/or heterocyclic and may optionally be substituted, for example, by halogen atoms.

Examples of carboxylic acids and their derivatives  
20 are succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, phthalic acid anhydride, tetrahydrophthalic acid anhydride, hexahydrophthalic acid anhydride, tetrachlorophthalic  
25 acid anhydride, endomethylene tetrahydrophthalic acid anhydride, glutaric acid anhydride, maleic acid, maleic acid anhydride, fumaric acid, dimerized and trimerized unsaturated fatty acids, optionally in admixture with monomeric unsaturated fatty acids, such as oleic acid,  
30 terephthalic acid dimethyl ester and terephthalic acid-bisglycol ester.

Examples of suitable polyhydric alcohols are ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4-and 2,3-butylene glycol, 1,6-hexanediol, 1,8-octanediol,  
35 neopentyl glycol, 1,4-bis-hydroxymethylcyclohexane,

2-methyl-1,3-propanediol, glycerol, trimethylol propane,  
1,2,6-hexanetriol, 1,2,4-butanetriol, trimethylol ethane,  
pentaerythritol, quinitol, mannitol, sorbitol, formitol,  
methyl glycoside, diethylene glycol, triethylene glycol,  
5 tetraethylene glycol and higher polyethylene glycols,  
dibutyl glycol and higher polybutylene glycols. The  
polyesters may contain terminal carboxyl groups.  
Polyesters of lactones, e.g., epsilon-caprolactone, or  
polyesters of hydroxycarboxylic acids, e.g.,  
10 omegahydroxycaproic acid, may also be used. Illustrative  
examples are polyester polyols available under the  
Urethhall trade name from C.P. Hall Company.

(e) Polythioethers, particularly the condensation  
products of thiodiglycol alone and/or with other glycols,  
15 dicarboxylic acids, formaldehyde, aminocarboxylic acids  
or amino alcohols. Depending on the co-components, the  
products can be, for example, polythio mixed ethers,  
polythioether esters or polythioether ester amides.

(f) Suitable polyacetals, including the compounds  
20 obtainable from glycols, such as diethylene glycol,  
triethylene glycol, 4,4'-diethoxy-  
diphenyldimethylmethane, hexanediol and formaldehyde.  
Polyacetals suitable for use in accordance with the  
present invention may also be obtained by polymerizing  
25 cyclic acetals such as trioxane (German  
Offenlegungsschrift No. 1,694,128).

(g) Polycarbonates containing hydroxyl groups  
obtained, for example, by reacting diols, such as 1,3-  
propanediol, 1,4-butanediol and/or 1,6-hexanediol,  
30 polyoxytetramethylene diol, diethylene glycol,  
triethylene glycol, tetraethylene glycol or thiodiglycol,  
with diaryl carbonates, for example, diphenyl carbonate,  
or phosgene (German Auglegeschrift No. 1,915,908 and U.S.  
Pat. Nos. 3,544,524, 3,867,350 and 4,054,597). An

illustrative example is Permapol KM 10-1733 available from ICI Stahl USA.

(h) Polyhydroxy (meth)acrylic resins, which are polymers and copolymers of mono esters of (meth)acrylic acid and polyhydric alcohols, useful for making polyester polyols (see (a), infra), e.g., homopolymers and copolymers of hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, and the like. Illustrative of such compounds are G-cure™ acrylic resin available from Henkel Corp., Minneapolis, MN, Desmophen™ A resins available from Mobay Corp., Pittsburgh, PA, and hydroxyl functional Acryloid™ resins, available from Rohm and Haas, Philadelphia, PA, and the like.

(i) Polyester amides and polyamides, including the predominantly linear condensates obtained, for example, from the reaction of polybasic saturated or unsaturated carboxylic acids or their anhydrides with polyhydric saturated or unsaturated amino alcohols, diamines, polyamines and mixtures thereof.

(j) Polyhydroxyl compounds already containing urethane or urea groups and optionally modified natural polyols, such as carbohydrates, for example, starch. Addition products of alkylene oxides with phenol/formaldehyde resins or even with urea/formaldehyde resins may also be used in accordance with the present invention.

(k) Modified polyhydroxyl compounds. Before they are used in the polyisocyanate/polyaddition process, the above-mentioned polyhydroxyl compounds may be modified in various ways. Thus, according to U.S. Pat. No. 3,849,515, a mixture of different polyhydroxyl compounds (for example, a polyether polyol and a polyester polyol) may be condensed by etherification in the presence of a strong acid to form a relatively high molecular weight

polyol which is made up of different segments attached through ether bridges.

- (k) polyamine compound. Suitable polyamines are those known in the art which contain more than one
- 5 primary or secondary amino group capable of reacting with isocyanate groups and have molecular weights from 400 to 100,000, preferably 800 to 20,000, with functionality from 2 to 6, preferably 2 to 3.

- Examples include polyoxyalkylene polyamines derived
- 10 from the amination of polyether polyols with the majority of the hydroxyl groups replaced by amine groups; polyamidoamines derived from dimerized fatty acids; amine terminated polybutadienes; amine terminated polytetrahydrofuran; amine terminated polybutadiene-
- 15 acrylonitrile copolymers; amine terminated polyethers obtained by hydrolysis of isocyanate prepolymers or by hydrogenation of cyanoethylated polyoxpropylene ethers, polyamines containing urea or amide or urethane moieties in their backbone; cyanoethylated amine terminated
- 20 polyoxypolypropylene ethers; polysiloxanes containing amino groups; tetramethylene oxide-di-aminobenzoates; polyethers containing aromatic amine end groups; Lewis acid-blocked primary or secondary aliphatic or aromatic amine groups, aldimines or ketimines of aliphatic
- 25 polyamines and mixtures of these.

- Useful classes of polyamines include aminopolyethers; polyamines containing urea or amide or urethane or ester moieties in their backbone, illustrative of these materials are the polyoxyalkylene
- 30 polyamines available as Jeffamine™ (the D, ED, DU, BUD and T series) from Texaco; polyamines containing aliphatic or cycloaliphatic organic compounds, such as polyamidoamines, amine terminated polyalkadiene copolymers, illustrative of the above materials are the
- 35 amine-terminated butadiene/acrylonitrile copolymers

available as Hycar™ from BF Goodrich; aminoalkyl terminated polydiorganosiloxanes, including polysiloxanes having a molecular weight of 400 to 100,000 which contain from 0.01 to 6 percent, preferably 0.05 to 1% by weight of nitrogen in the form of primary or secondary amino groups; illustrative of these materials is the difunctional aminopropyl-terminated polydimethylsiloxane formed by reaction of aminopropyl trialkoxysilane with octamethyl cyclotetrasiloxane, and polyethers containing aromatic amine end groups such as anthranilic acid esters.

Other suitable aromatic polyamines include those containing urea or urethane or amide or ester moieties in their backbone. Commercially available examples are the polytetramethyleneoxide-di-p-aminobenzoates available as Polamine™ from Air Products.

In addition to the above polyols and polyamines, the composition of the invention may also contain lower molecular weight, reactive, chain-extending or crosslinking compounds having molecular weights of 400 or less and containing at least two isocyanate-reactive hydrogen atoms.

The amount of chain extending agent required varies with the desired crosslink density in the cured form, but typically, minor amounts are used. Useful examples include polyhydric alcohols, alkanol amines, primary or secondary aliphatic, cycloaliphatic, aromatic, araliphatic or heterocyclic amines, low molecular weight amine-initiated polyether polyols, ricinoleic derivatives, hydroxyl containing organophosphates, poly-(oxyalkylene)amines, substituted hydrazines and hydrazides, and mixtures thereof.

Suitable aromatic amine chain extenders include the sterically hindered aromatic polyamines, preferably diamines, which contain linear or branched alkyl

substituents or halogen or similar substituents in the ortho position to the amino groups. Aromatic polyamines also include amines in which the amino group is attached to heterocyclic radicals of aromatic character. Examples  
5 include 1-methyl-3,5-diethyl-2,6-diamino benzene; 4,4'-methylene bis(2-chloroaniline); 4,4'-diamino-diphenyl sulfone; isobutyl-3,5-diamino-4-chlorobenzoate, NaCl blocked methylene bis (aniline), and the like.

In addition, aliphatic amine-containing chain  
10 extenders can be employed. Such compounds include ethylene diamine, methylene-bis(cyclohexyl amine), N,N'-ditertiary-butyl ethylenediamine, amino ethyl piperazine, meta-tetramethylenexylene diamine, and the like. Illustrative of the above materials is 5-amino-1,3,3-  
15 trimethyl cyclohexane-methaneamine (isophorone diamine) Vestamin™ available from Huls.

Low molecular weight hydroxyl terminated compounds can be utilized as chain extenders. Examples of such polyols are N,N-bis (2-hydroxypropyl)aniline, 1,6-  
20 hexanediol, tripropyleneglycol, trimethylol propane, 1,4-dihydroxyl cyclohexane, diethanolamine, 1,4-bis(hydroxyethyl)piperazine, and the like. It is also possible to use diols containing additional groups, for example, bis-(2-hydroxylpropyl)-isophthalate,  
25 polycaprolactone glycol, 1,6-hexamethylene-bis-(2-hydroxyethylurethane), 4,4'-diphenylmethane-bis-(2-hydroxyethyl urea), ethylene glycol mono-ricinoleate, and the like. Illustrative of the above materials are diethyl-N,N-bis(2-hydroxyethyl) amino methylphosphonate,  
30 Fyrol™, available from Akzo; pentaethrythritol monoricinoleate, Conacure™ available from Conap; propylene oxide adduct of trimethylolpropane, Pluracol™, available from BASF; and polyethylene or polypropylene

oxide adducts of ethylene diamine, also available under the Pluracol™ or Quadrol™ trade name.

Elastomers of the invention may also contain a plasticizing system having one or more extenders or  
5 plasticizers. The plasticizing system is preferably selected so as to be essentially inert with polyurethane/polyurea reaction products and substantially non-exuding.

Useful plasticizers include mono-, di-, and poly-  
10 esters, (such as trimellitates, phthalates, benzoates, polymeric polyesters, castor oil derivatives, and the like) and mixtures thereof. Flame retardency of the elastomers can be improved by the use of halogen/or phosphorus containing compounds, for example, halogenated  
15 phosphate or polyphosphate esters, halogenated organic phosphonates, and halogenated hydrocarbons. These flame retardants can be employed along with hydroxyalkyl phosphonate esters and/or appropriate fillers to impart the desired degree of fire retardancy. Illustrative of  
20 the above materials is Plasthall P643 from C.P. Hall company and glyceryl tri(acetyl ricinoleate) available under the Flexricin™ trade name from CasChem.

Any conventional catalyst used in the preparation of polyurethanes may be employed herein. Typically, from  
25 0.005% to 5.0%, preferably 0.05 to 2.5% by weight of the total reactants of catalyst is added to facilitate the reaction.

Useful catalysts include organometallic chelates, alcoholates, phenolates, and salts of organic acids,  
30 tertiary amines, organic tin compounds, bicyclic amidines, silaamines, acidic metal salts of strong acids, tertiary phosphines, alkali and alkali earth metal hydroxides, and the like, and combinations thereof.

Exemplary organometallic catalysts include  
35 catalytically active compounds of tin, iron, mercury,



bismuth, zinc, manganese, lead, copper, cobalt, titanium, antimony, cadmium, aluminum, nickel, cerium, vanadium, and the like. Illustrative of the above compounds would be stannous octoate, bismuth neodecanoate, lead naphthenate, phenylmercuric benzoate, lead ethylhexanoate, and ferric acetyl acetate. Suitable organic tin compounds include tin (II) salts of carboxylic acids such as tin ethylhexanoate and tin laurate and the tin (IV) compounds, such as dibutyl tin dilaurate, dibutyl tin oxide, dimethyl-tin (IV)-bis-thiolauryl, dibutyl tin-bis-thioglycolic acid octyl ester, and the like. An illustrative example is BiCat 8, available from Shephard Chemical.

Useful tertiary amines include, for example, N-methyl morpholine, bis(2-dimethylaminoethyl) ether, 1-methyl-4-dimethylaminoethyl piperazine, dimethylbenzylamine, triethylamine, 1,8-diazabicyclo(5,4,0)-undec-7-ene (DBU) and salts thereof, 1,4-diazabicyclo(2,2,2) octane, triethylene diamine, and the like.

One preferred embodiment of the invention also contains hollow microspheres made of silicate, phenolic, glass, epoxy, vinylidene chloride copolymers, flyash, carbon, clay and the like. They are typically roughly spherical, ranging in particle size from about 0.5 to 300 microns. The microspheres may be glass, e.g., Scotchlite™, available from Minnesota Mining and Manufacturing Company (3M) or polymeric, e.g., Expancel™ 551DE, available from Nobel Industries, UCAR microballoons, available from Union Carbide Corp., and Dualite™ M6001AE, available from Pierce and Stevens Corp.; or ceramic, e.g., Zeeosphere™ X-40, manufactured by Zeelan Industries. Such microspheres may also be treated with a coupling or wetting agent such as a silane, e.g., 3-glycidoxypropyl trimethoxy silane, or an

organo-chromium or titanium or zirconium complex to enable the resin to effectively wet the microspheres.

Additional fillers or combinations of fillers may also be present, such as glass fibers, graphite fibers, fibrous materials emanating from an organic polymer, carbon black, mica, aluminum oxide hydrates, various silicates or carbonates or clays, fumed silica and the like. The term "filler" is used herein to include all solid additives including particulate matter or fibrous matter, present in the composition. Illustrative of the above materials is a fumed silica available under the trade name Cab-O-Sil™ from Cabot.

In one embodiment, expandable sealants may be made from compositions of the invention by adding expandable microspheres to the composition. The sealant may be a one-part sealant which is activated by the application of heat, or it may be a two-part sealant which exotherms upon reaction, providing the necessary heat to cause expansion of the microspheres. Such sealants are especially useful as sealants in devices which have heated process steps. The unexpanded encapsulant can be placed against one side of an area to be filled prior to the heated process step. As the device is heated, the elastomer sealant will expand to fill the area as desired. In one application, the elastomer is placed inside an automobile body where sealing is desired. A small amount is placed in a bead against the wall or seam. When the automobile is subjected to heat during the painting process, the seal will expand to fill the area and seal the seam.

Expandable microspheres useful in such an embodiment include those available as Expancel™ "WU" or "DU" microspheres from Nobel Industries (designating whether the unexpanded microspheres are wet or dry), including Expancel™ 642 DU, 820 DU, 820WU and the like, providing

the Expancel™ "WU" grades are dried before use to remove the moisture.

Although the crosslinking reactions to prepare the elastomeric compositions of the present invention are preferably conducted at or near ambient temperature, one skilled in the art may accelerate the reaction rate if desired, by the application of elevated temperatures. Reaction at elevated temperatures may be necessary if blocked isocyanates or expandable microspheres are used.

10 It is also possible to add other additives, such as wetting agents, UV absorbers, mold release agents, drying agents, such as molecular sieves, fungicides, oxidation preventatives or any other additive as necessary. As oxidation preventatives, there can be used hindered  
15 phenols, for example, Irganox™ 1010, Tetrakis methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)methane, and Irganox™ 1076, Octadecyl-8-(3,5-tert-butyl-4-hydroxyphenol) propionate, all available from Ciba-Geigy Company.

20 Although the polymers of this invention show excellent hydrolytic stability without stabilizers, it may be useful at times to include a carbodiimide, such as Staboxol from Miles Chemical Company, in 0.2 to 3.0, preferably from 0.5 to 1.0 parts by weight based upon 100  
25 parts by weight of said urethane polymer.

In order to make elastomers of the invention, the isocyanate reactive blend is mixed together. Other additives, fillers and the catalyst are mixed. The isocyanate is then added to the blend and the elastomer  
30 is then cured, either at ambient temperature or elevated temperature, as desired.

Elastomers of the present invention are suitable for applications in which the polymer is exposed to hydrocarbon fuels, particularly kerosene. Contemplated  
35 uses include sealants, linings, coatings, end seals,

gaskets, bushings, sleeves, connector sealants, sound attenuation devices, vibration damping devices, encapsulants, potting materials, and the like. Seals include e.g., endcaps for fuel filters, pipe seals, sealants that fill construction gaps and the like, o-rings, gaskets, end-seals or gaskets for electrical/telecommunication splice cases or closures for wires or wire pairs or fiber optic strands for signal or electrical transmission, seals for automotive structural components, and the like.

Connector sealants include, e.g., sealants used to fill connecting devices for telecommunication, electrical and/or automotive applications which provide kerosene-resistant water-proof electrical or signal connectors, fillers for telecommunication terminal block caps, and the like.

Linings include liners for hoses, pipes and containers, and the like. Encapsulants or potting materials include fillers for electrical or signal transmission devices such as splice closures, service branch-out assemblies, cables, and the like. Sealants are also useful for containing fuel, as part of a fuel tank.

Where use in signal transmission devices is desired, the elastomer is molded into the desired configuration or poured into a protective housing, and cured under the conditions required for the specific composition used.

Sealants of the present invention are particularly useful for cable splice closures that provide a protective barrier for sealing splice cases or closures for wires or wire pairs or fiber optic fibers or other outside telecommunication apparatus from damage caused by environmental exposure. Historically, such sealants were based on butyl rubber and do not perform well in fuel contaminated environments commonly found in manholes.

The elastomeric sealants of the invention are expandable with the motion of connected structural components and thus have use in automotive assembly. Recently the automotive and aircraft industries have concentrated on efforts to reduce the overall weight. Light weight sealant materials are described in this invention for those applications where weight is a factor.

Figure 1 teaches that propylene oxide based polyurethanes of the invention exhibit a surprising correlation between the percent weight change in kerosene and the total weight percent of organic poly adduct and/or polycondensate dispersion particles and epoxy compounds present, based on the total polyurethane formulation. The percent weight gain in kerosene was shown to be reduced from over 50 percent by weight to less than 10 percent.

Useful kerosene resistant viscoelastic elastomers can be obtained even at extremely low isocyanate indices, e.g., even to 10 or below. The resulting materials have excellent kerosene resistance and hydrolytic stability combined with excellent low temperature flexibility.

By the proper balancing of the nature and reactivity of the isocyanate reactive compounds, polypropylene ether polyols containing polyadducts and polycondensate dispersions along with epoxy compounds, elastomers may be prepared having viscoelastic characteristics ranging from firm elastomers to jelly-like sealants, as desired for varying applications.

The following examples are for illustrative purposes only, and are not limiting to the scope of the invention. Variations within the claimed scope may easily be rendered by one skilled in the art. All parts, percents, and ratios are by weight unless otherwise indicated. A

dashed line indicates that a test was not run in a particular example.

#### Test Methods

5

##### Shore OO Hardness

Shore OO hardness was tested according to the American Society of Test Methods, Test Method "D2240".

##### Tensile Strength and Elongation

10

Tensile Strength and elongation were measured according to ASTM Test Method "D-412".

##### Kerosene Resistance

The kerosene resistance was measured by the swelling  
15 when placed in a hydrocarbon. The exemplary hydrocarbon is kerosene. To demonstrate kerosene resistance; 3 tensile dumbbells (cut by die C according to ASTM D412) were immersed for 24 hours (1 day) at 37.8°C (100°F). This procedure was chosen to expose the maximum surface  
20 area to the kerosene. After 24 hours, the samples were rinsed in water and wiped dry. Swelling after soaking was measured by weighing the sample before and after soaking to the nearest milligram and is expressed as the percent change in weight by the following equation:

25

$$\text{Percent weight change} = (w_1 - w) / w \times 100$$

where  $w$  is the weight of the specimen before the immersion and  $w_1$  is that after the immersion. Practice of  
30 this invention preferably produces a polyurethane or polyurethane/urea polymer exhibiting a percent weight gain of less than 30 percent, more preferably less than 20 percent, and most preferably less than 10 percent.

This test requires the use of fresh kerosene for each test in order to achieve accurate results. When run accurately, the data show variation of 5% or less.

5                                    Hydrolytic Stability

In order to evaluate the resistance to water, three specimens 2.5 by 5 by 1.3 cm thick were weighed to the nearest milligram and then boiled in water, thus 100°C (212°F), at constant volume (reflux) for 1 week (7 days ±  
10 2 hours). The samples were allowed to cool in the water for 2 hours, removed, blotted dry and maintained at 75 ± 2°F for 2 hours prior to weighing to the nearest milligram. The swelling after soaking is expressed as the percent weight change between before and after the  
15 immersion by the following equation:

$$\text{Percent weight change} = (w_1 - w) / w \times 100$$

where w is the weight of the specimen before the  
20 immersion and w<sub>1</sub> is that after the immersion. The samples preferably maintained the original shape and did not disintegrate and had a percent weight gain of less than 15 percent, preferably less than 10 percent and most preferably of less than 5 percent.

25

One-Quarter Cone Hardness

Hardness was tested using ASTM Test Method "D1403".

Heat Aging

30        Dry heat aging was tested by heating a thin polymer slab for 18 hours on a Teflon™ coated plate to 104.4°C (220°F) in a vented oven. Syneresis or its absence was observed visually, and dumbbells were then cut for elongation testing.

Glossary

The following glossary lists the commercially available components used in the following examples. The function of each component is also listed. Function of  
5 the component is defined as follows:

<u>Function</u>	<u>Abbreviation</u>
Isocyanate	I
Blocked isocyanate	BI
Polyamine crosslinking agent	PACA
Alcohol Crosslinking Agent	ACA
Plasticizer	P
Polymer Polyol Crosslinking Agent	PPCA
Microsphere filler	M
Microsphere filler, expanding	MEF
Filler	F
Catalyst	C
Antioxidant	A
Epoxy resin	E



MATERIAL	DESCRIPTION	AVERAGE EQUIVALENT WEIGHT	SOURCE	FUNCTION
Vestanat IPDI	isophorone-diisocyanate (3-isocyanato methyl -3, 5, 5, -trimethylcyclohexyl - Isocyanate)	111	Huls	I
Mondur CD	Carbodiimide derivative of 4, 4' - diphenylmethane diisocyanate	144	Miles	I
Desmodur W	4,4' methylene-bis(cyclohexyl) isocyanate, hydrogenated MDI or H <sub>12</sub> MDI	132	Miles	I
Cyanamid TMXDI (meta)	Meta-tetramethylylene diisocyanate -	122	Cyanamid	I
Desmocup 11A	100% solids 4-nonylphenol blocked isocyanate prepolymer with 2.6 average functionality with 2.4% available isocyanate	1750	Miles	BI
Multranol 9151	Polyurea dispersion in ethylene oxide capped polypropylene oxide triol with terminal unsaturation (meg/gm) of 0.06	2003	Miles	PPCA
Multranol 9238	Polyurea dispersion in ethylene oxide capped polypropylene oxide triol - Polymer polyol	2003	Miles	PPCA
Arcol Polymer Polyol 34-28	Dispersion of 11% polyacrylonitrile/10% polystyrene in ethylene oxide capped polypropylene oxide triol	2003	Arco	PPCA
Pluracol 994LV	Dispersion of 40% polyacrylonitrile/polystyrene in polypropoxylated glycerin triol-polymer polyol	1935	BASF	PPCA
Poly-G-85-28	Ethylene oxide capped polypropylene oxide of about 6000 molecular weight	2003	Olin	ACA
Poly-L(R)-385-29	Ethylene oxide capped polypropylene oxide of about 5800 molecular weight with terminal unsaturation (meg/g) of 0.017	1935	Olin	ACA
Capa 316	Polycaprolactone tetrol of about 1000 molecular weight	257	Interox	ACA

MATERIAL	DESCRIPTION	AVERAGE EQUIVALENT WEIGHT	SOURCE	FUNCTION
Arco LHT 28	Polypropylene oxide triol	2003	Arco	ACA
USP Castor Oil	Vegetable oil of about 70% glycerin triricinolein and about 30% glycerol diricinolein mono-oleate or monolinoleate and hydroxy functionality of about 2.7	344	United Catalyst	ACA
Urethall 4050-35	Polyester polyol of about 3000 molecular weight with average functionality of about 2	1484	C.P.Hall	ACA
Urethall 4150-55	Polyester polyol of about 2000 molecular weight with average functionality of about 2.8	1020	C.P. Hall	ACA
Permapol KM 10-1733	Aliphatic polycarbonate diol	431	ICI-Stahl	ACA
Jeffamine T403	Polypropylene oxide triamine of about 400 molecular weight	81	Texaco	PACA
MXDA	Meta-xylylene diamine of about 136 molecular weight	68	Aldrich	PACA
Plasthall P643	Adipate polyester of about 2000 molecular weight	NA	C.P.Hall	P
PDMS Diamine	Polydimethylsiloxane diamine. Average molecular weight of about 20,000	5000	3M	PACA
Jeffamine T5000	Polypropylene oxide triamine 5000 molecular weight	833	Texaco	PACA
Hycar 13000 x 21	Difunctional secondary amine terminated butadiene acrylonitrile copolymer. Average molecular weight of about 2400	1200	BF Goodrich	PACA
Polamine 2000	Polytetramethylene oxide-di-p-aminobenzoate of about 2200 molecular weight	1090	Air products	PACA

MATERIAL	DESCRIPTION	AVERAGE EQUIVALENT WEIGHT	SOURCE	FUNCTION
BiCat 8	Bismuth/Zinc Neodecanoate	N/A	Shephard	C
Irganox 1076	Octadecyl 8(3,5-t-butyl-4-hydroxyphenyl) propionate-antioxidant	N/A	Ciba-Geigy	A
Dualite MG001AE	Hollow composite polymeric microspheres coated with calcium carbonate of about 50 micron particle size having a density of about 0.13 gm/cc	N/A	Pierce and Stevens	M
Expancel 551 DU	Hollow unexpanded microspheres composed of a vinylidene chloride/acrylonitrile copolymer of about 10 microns, containing a blowing agent, Isobutane, that expands to about 35 microns at about 142-150°C	N/A	Nobel Ind.	MEF
Epon 828	Bisphenol A diglycidylether epoxy resin	188	Shell	E
Epon 826	Bisphenol A diglycidylether epoxy resin	182	Shell	E
D.E.N. 431	Phenolformaldehyde polyglycidyl ether epoxy resin	178.5	Dow	E
D.E.R. 736	Polypropylene oxide diglycidyl ether epoxy resin	190	Dow	E
Scotchlite™ GB 522/400	Hollow glass microspheres; density 0.22 g/cc, size 40µm	N/A	3M	M

Production of the Epoxy ResinPolymer Polyol DispersionsPreparation A

A mixture of 800.0 gms Poly-L-385-29, 160.1 gms Epon  
5 826 and 39.9 gms meta-xylene diamine (Epoxy/amine  
equivalence ratio = 1.5), was stirred about three minutes  
until the mixture was clear. The mixture was then placed  
in a glass bottle under nitrogen into a 50°C (122°F) oven  
for 48 hours during which the epoxy resin and epoxy  
10 reactive curing agent reacted to give a dispersion. The  
solids content was calculated to be 20 percent by adding  
the weight of the epoxy resin and the m-xylene diamine  
divided by the weight of the total reaction mixture. The  
equivalent weight was calculated to be 2430 based on the  
15 hydroxyl number of 28.86 for the Poly-L-385-29 base  
polyol and 1000 gms of polymer polyol dispersion.

Preparation B

Preparation B was prepared in a like manner, using  
20 800 gms Arcol LHT-28, 160.1 gms Epon 826 and 39.9 gms  
meta-xylene diamine (Epoxy/amine equivalence ratio =  
1.5). The calculated solids content of the dispersion  
was 20 percent and the calculated equivalent weight was  
2504.

25

Preparation C

Preparation C was prepared in a like manner, using  
820 gms castor oil, 144.1 gms Epon 826 and 35.9 gms meta-  
xylene diamine (Epoxy/amine equivalence ratio = 1.5).  
30 The calculated solids content of the dispersion was 18  
percent and the calculated equivalent weight was 419.

#### Preparation D

Preparation D was prepared in a like manner, using 650 gms of Poly-L-385-29, 269.3 gms Epon™ 826, and 80.7 gms meta-xylenediamine (Epoxy/amine equivalence ratio = 1.25). The calculated solids content of the dispersion was 35% and the calculated equivalent weight was 3138.

#### Preparation E

Preparation E was prepared in a like manner, using 870 gms of castor oil, 95.9 gms Epon™ 826, and 34.5 gm meta-xylenediamine (Epoxy/amine equivalence ratio = 1.05). The calculated solids content of the dispersion was 13% and the calculated equivalent weight was 395.

15

#### Preparation F

Preparation F was prepared in a like manner, using 800 gms of Poly-G-85-29, 153.9 gms Epon™ 826, and 46.1 gms meta-xylenediamine (Epoxy/amine equivalence ratio = 1.25). The calculated solids content of the dispersion was 20% and the calculated equivalent weight was 2526.

#### Preparation G

Preparation G was prepared in a like manner, using 700 gms of Poly-G-85-29, 230.9 gms Epon™ 826, and 69.1 gms meta-xylenediamine (Epoxy/amine equivalence ratio = 1.25). The calculated solids content of the dispersion was 30% and the calculated equivalent weight was 2904.

#### Examples

30

#### Elastomer Making Procedure

The same general procedure was followed for all of the examples. The isocyanate reactive blend was prepared

and mixed from the stated polyamines, polyols, catalysts, microspheres, fillers, etc. The isocyanate was then added to the blend, and the reactants were quickly mixed mechanically and poured into a mold. The materials were then cured under one of several conditions. Certain materials were cured overnight at ambient room temperature. This was designated as Cure "A".

To speed the curing, some molds were heated for one and one half hours at 76.7°C (170°F), and then allowed to sit overnight. This was designated as cure "B".

Finally, for examples 16 and 17, which involved blocked isocyanates, the molds were placed in a vented oven and heated for forty-five minutes at 124°C (256°F). This was designated cure "C".

15 All microspheres or fillers were dried at least 18 hours at 71.1°C (160°F).

#### Comparative Examples C1-C7

The comparative examples C1-C7 in Table I were prepared to confirm the fact that largely polypropylene ether based polyurethanes are not kerosene resistant and swell in kerosene, with percent weight gains of greater than 45 percent by weight after immersion of 24 hours at 100°F. Comparative examples C1 and C2 show that this is the case when either aliphatic or aromatic polyisocyanates are used. Comparative example C3 and C4 indicate that the kerosene resistance becomes worse as the isocyanate index was lowered to about 65 as the percent weight gain in kerosene increased. When a polymer polyol dispersion (Multranol™ 9238 or Arcol 34-28 polymer polyol) is incorporated into the polyurethane formulation, its use alone is not sufficient to improve

the kerosene resistance as shown by comparative examples C5 and C6. The use of 15 percent epoxy compound, Epon™ 826, alone in a polyurethane formulation also did not improve the kerosene resistance for comparative example 5 C7.

Further, as can be seen in Table IA, comparative examples similar to examples of the invention, but lacking either the dispersion or the epoxy, do not perform as well, particularly with regard to kerosene resistance, as do elastomers of the invention.

Table I

Components	C1	C2	C3	C4	C5	C6	C7
Vestanat IPDI	5.3	--	2.9	--	--	5.0	--
Mondur CD	--	6.5	--	--	--	--	5.5
Cyanamid-m-TMXDI	--	--	--	3.1	--	--	--
Desmodur W	--	--	--	--	5.9	--	--
Poly-L(R)-385-29	92.7	--	50.5	49.1	--	--	--
Arcol LHT-28	--	91.5	44.6	45.8	--	--	77.5
Poly-G-85-28	--	--	--	--	44.6	45.5	--
Multranol 9238	--	--	--	--	47.5	--	--
Arcol 34-28	--	--	--	--	--	47.5	--
Epon 826	--	--	--	--	--	--	15.0
BiCat 8	0.2	0.05	0.2	0.2	0.2	0.2	0.05
Irganox 1076	1.8	1.95	1.8	1.8	1.8	1.8	1.95
Isocyanate Index	99.6	99.6	65.0	65.6	97.2	96.9	99.5
Kerosene Immersion - 24 hrs. 38°C (100°F) - % Weight Change	+51.4	+46.1	+68.0	+77.0	+53.2	+50.5	+66.5

TABLE 1A

Components	C1	Ex. 1	C6	Ex. 20	C5	Ex. 21
Vestanat IPDI	5.3	3.4	5.0	3.5	--	--
Desmodur W	--	--	--	--	5.9	3.6
Poly -L(R)-385-29	92.7	--	--	--	--	--
Preparation A - 20% Epoxy resin dispersion in Poly-L(R)-385-29	--	74.6	--	--	--	--
Poly-G-85-28	--	--	45.5	--	44.6	--
Arcol 34-28	--	--	47.5	28.6	--	--
Multranol 9238	--	--	--	--	47.5	16.0
Preparation F - 20% Epoxy resin dispersion in Poly-G-85-28	--	--	--	43.9	--	--
Preparation G - 30% Epoxy resin dispersion in Poly-G-85-28	--	--	--	--	--	56.4
Epon 826	--	20.0	--	22.0	--	22.0
BiCat 8	0.2	0.2	0.2	0.2	0.2	0.2
Irganox 1076	1.8	1.8	1.8	1.8	1.8	1.8
Isocyanate Index	99.6	99.7	96.9	99.5	97.2	99.5
Kerosene Immersion -24 hrs. 38°C (100°F) % Weight Change	+51.4	+9.9	+50.5	+14.2	+53.2	+14.9

Examples 1-19

- 5        Examples 1-19 were prepared according to the above described procedure. Excellent kerosene resistance was obtained by an unexpected synergism between polypropylene ether polyols containing polyadduct and/or polycondensate dispersions, i.e., polymer polyols, and epoxy compounds.
- 10      Examples 1 to 4 of Table II indicate the improvement in kerosene resistance from the incorporation of a polymer polyol, preparation A and/or preparation B, and an epoxy compound, Epon 826. Each of these examples was based on the same polypropylene ether polyols as comparative
- 15      examples C1 and C2. Thus, in example 1, the polymer polyol dispersion was prepared in a base polyol of Poly-L-385-29 which is the same largely propylene ether polyol used in comparative example C1. However, the combination



of the polymer polyol and the epoxy compound led to a percent weight gain in kerosene of 9.9 for example 1, an improvement to about one fifth that obtained with C1. Examples 1 to 4 offer the results of kerosene percent weight gain as the total weight percent of the organic polyadduct and/or polycondensate dispersion particles and epoxy compounds present (based on the total polyurethane formulation) varies from 23 percent to 35 percent. The weight percent of the organic polyadduct and/or polycondensate dispersion particles may be obtained by multiplying the percent solids (dispersion particles) in the polymer polyol times the weight percent of the polymer polyol present in the total polyurethane or polyurethane/urea formulation. This value is then added to the weight of the epoxy compound present in the total polyurethane or polyurethane/urea formulation. Thus, for example 1, the polymer polyol contains a 20% polyadduct dispersion and 20 weight percent of Epon 826 so would have a total of  $0.2 (74.6) + 20.0$  or 34.9 weight percent.

Following the teachings of the present invention for a polyurethane based only on largely propylene oxide polyols, Figure 1 indicates that the percent weight gains in kerosene can be reduced to less than 10 percent when the total weight percent of organic polyadduct and/or polycondensate dispersion particles and epoxy compounds approaches 35 percent. It should be appreciated by those skilled in the art that following the present teachings, this critical value decreases when a polyester polyol or polycarbonate polyol or the like is included in the polyurethane or polyurethane/urea formulations.

Note that Examples 1-4 also retain excellent low temperature properties, with glass transition temperatures ( $T_g$ ) of below  $-65^{\circ}\text{F}$  ( $-54^{\circ}\text{C}$ ) from the TMA

scans. In addition, the percent weight gain in boiling water after 1 week were all below 4 percent thus reflecting the excellent hydrolytic stability.

Example 5 of Table II incorporates a polyester polyol (Urethhall 4150-55) in the polyurethane formulation to yield excellent kerosene resistance along with the low temperature properties, i.e., low Tg, and hydrolytic stability expected for the polypropylene ether polyol also present. An inert polyester plasticizer, Plasthall P643, was included in Example 6 of Table II along with a polycarbonate polyol (Permapol KM 10-1733). Example 7 of Table III demonstrates the use of an aliphatic epoxy compound, i.e., D.E.R. 736, instead of the aromatic Epon 826 epoxy compound.

Surprisingly, examples 8 to 15 and 18-19 of Tables III and IV demonstrate that useful kerosene resistant viscoelastic elastomers can be obtained even at extremely low isocyanate indices, e.g., even to 10 to below. Tables II to V also show elastomers made from varying systems to demonstrate the broad nature of the invention. Example 8 has an isocyanate index below 10 yet still shows excellent kerosene resistance. The examples also demonstrate the range of polyisocyanates useful in systems of the invention. Aliphatic polyisocyanates are used in Examples 1 to 8 and 11 to 14. Examples 9, 10 and 15 use aromatic polyisocyanates, and blocked isocyanates are used in 16 and 17. Various amines are utilized; an aliphatic triamine in example 11, an aromatic diamine in Example 12, a secondary aliphatic diamine in Example 13, and a polydimethylsiloxane diamine in Example 14. A Novalak type epoxy compound was used in Examples 12, 13 and 15. Likewise, polymer polyols have been varied throughout the examples. Elasticity remained for the

polyisocyanates or polyisocyanate/ureas with low isocyanate indices even after dry heat aging of the elastomers at 104°C, and no syneresis occurred under those conditions.

- 5        Light weight elastomers were prepared containing hollow microspheres as demonstrated in examples 8, 10 to 14, 16 and 19.

Unexpanded hollow polymeric microspheres (Expancel 551DU in Exp. 16) were also expanded during a heat cure  
10 with blocked isocyanates, to give an expanding sealant as described earlier. Example 16 expanded about 100 percent.

Example 19 demonstrates a very soft sealant suitable for a connector sealant.

- 15        The most preferred largely polypropylene ether polyols are polymers of propylene oxide or mixtures of propylene oxide and ethylene oxide, in which the oxypropylene units derived from the propylene oxide constitute at least 50%, more preferably at least 65%,  
20 most preferably at least 75% by weight of the polyether.

In addition, the polypropylene oxide polyols should have a total unsaturation content of less than 0.08, preferably less than 0.06, more preferably less than 0.04 and most preferably less than 0.02 milliequivalents/gram  
25 polyol.

Table II

Components	1	2	3	4	5	6
Vestanat IPDI	3.4	4.0	3.8	2.8	4.6	--
Desmodur W	--	--	--	--	--	6.5
Preparation A - 20% Epoxy resin dispersion in Poly-L-385-29	74.6	31.0	84.2	61.2	--	--
Preparation B - 20% Epoxy resin dispersion in Arcol LHT-28	--	--	--	29.0	--	--
Multranol 9151	--	48.0	--	--	62.2	51.5
Urethall 4150-55	--	--	--	--	11.2	--
Plasthall P643	--	--	--	--	--	10.0
Permapol KM 10-1733	--	--	--	--	--	10.0
BiCAT 8	0.2	0.2	0.2	0.2	0.1	0.2
Irganox 1076	1.8	1.8	1.8	1.8	1.9	1.8
Epon 826	20.0	15.0	10.0	5.0	20.0	20.0
Cure	B	B	B	B	A	A
Isocyanate Index	99.7	98.0	98.7	68.5	98.5	100.7
Kerosene Immersion - 24 hrs. 38°C (100°F) - % Weight Change	+9.9	+14.8	+18.8	+30.0	+0.4	+9.0
T <sub>g</sub> (from TMA) °C (°F)	-54.0 (-65.0)	-54.1 (-65.4)	-56.5 (-69.8)	-53.6 (-64.4)	-54.0 (-65.2)	-45.7 (-50.3)
Hardness, Shore 00	71.1	79.6	75.8	54.2	74.0	48.8
Hardness, 1/4 Cone	5.0	2.0	3.4	10.2	5.0	11.6
Density, gm/cc	--	--	--	--	--	--
Tensile Strength, N/cm <sup>2</sup> (psi)	92.9 (132.2)	129.9 (184.8)	80.9 (115.1)	46.8 (66.6)	103.9 (147.8)	142.8 (203.1)
% Elongation, Initial	231.8	142.1	134.2	284.4	222.9	579.7
Tear Strength, N/cm (lb/in)	51.5 (29.4)	63.6 (36.3)	45.9 (26.2)	38.2 (21.8)	49.0 (28.0)	41.3 (23.6)
After dry heat aging -18 hrs. 104.4°C.						
% Elongation	254.9	144.6	137.7	349.7	278.3	634.6
Syneresis	None	None	None	None	None	None
Hydrolytic Stability - 7 days. 100°C. % Weight Change	+1.1	+3.9	+3.7	+3.4	+3.6	-1.4

Table III

Components	7	8	9	10	11
Vestanat IPDI	4.9	1.7	--	--	2.8
Mondur CD	--	--	4.1	2.9	--
Multranol 9151	61.4	30.6	57.5	40.6	43.1
Urethhall 4050-35	10.0	--	--	--	--
Capa 316	1.7	--	--	--	--
Preparation C - 18% Epoxy resin dispersion in Castor Oil	--	59.7	--	--	--
Castor Oil	--	--	16.4	28.5	26.2
Jeffamine T5000	--	--	--	--	6.4
D.E.R. 736	20.0	--	--	--	--
Epon 826	--	--	20.0	20.0	--
Epon 828	--	--	--	--	13.5
BiCAT 8	0.1	0.4	0.05	0.1	0.4
Irganox 1076	1.9	1.6	1.95	1.9	1.6
Dualite M6001AE	--	6.0	--	6.0	6.0
Cure	B	B	B	B	A
Isocyanate Index	100.2	9.7	37.6	19.7	23.9
Kerosene Immersion - 24 hrs. 38°C (100°F) - % Weight Change	+11.7	+3.8	+4.3	+0.6	+12.6
T <sub>g</sub> (from TMA) °C (°F)	-61.0 (-77.8)	-55.9 (-68.6)	-48.7 (-55.7)	-55.8 (-68.4)	-54.3 (-65.7)
Hardness, Shore 00	53.0	25.0	62.9	45.0	41.0
Hardness, 1/4 Cone	13.0	20.6	5.8	16.7	3.0
Density, gm/cc	--	0.607	--	0.553	--
Tensile Strength, N/cm <sup>2</sup> (lb/in)	112.8 (160.4)	19.3 (27.5)	94.3 (134.2)	25.5 (36.3)	34.5 (49.1)
% Elongation, Initial	351.8	290.3	258.5	346.0	272.4
Tear Strength, N/cm (lb/in)	50.1 (28.6)	14.4 (8.2)	38.5 (22.0)	18.6 (10.6)	28.7 (16.4)
After dry heat aging - 18 hrs. 104.4°C.	346.2	272.4	262.5	491.8	359.2
% Elongation Syneresis	None	None	None	None	None
Hydrolytic Stability - 7 days. 100°C. % Weight Change	+1.9	--	+2.5	+4.6	+8.0

Table IV

Components	12	13	14	15
Cyanamid n-TMXDI	4.0	3.7	--	--
Desmodur W	--	--	3.6	--
Mondur CD	--	--	--	3.0
Multranol 9151	59.0	54.5	53.2	42.1
Castor Oil	5.4	10.1	--	--
Preparation C - 18% Epoxy Resin Dispersion in Castor Oil	--	--	9.4	--
Polamine 2000	3.6	--	--	--
Hycar 1300 x 21	--	3.7	--	--
PDMS diamine	--	--	6.8	--
Epon 826	--	--	19.0	--
D.E.N. 431	20.0	20.0	--	20.0
Pluracol 994LV	--	--	--	32.9
BiCAT 8	0.2	0.2	0.2	0.02
Irganox 1076	1.8	1.8	1.8	1.98
Dualite M6001AE	6.0	6.0	6.0	--
Cure	B	A	B	B
Isocyanate Index	63.3	50.8	54.9	55.2
Kerosene Immersion - 24 hrs. 38°C (100°F) - % Weight Change	+11.2	+12.9	+13.9	+13.2
T <sub>g</sub> (from TMA) °C (°F)	-64.3 (-83.7)	-60.0 (-76.0)	-49.2 (-56.5)	-55.6 (-68.0)
Hardness. Shore 00	60.4	64.4	74.6	65.0
Hardness. 1/4 Cone	4.5	3.0	4.8	9.0
Density. gm/cc	0.58	0.58	0.697	--
Tensile Strength. N/cm <sup>2</sup> (psi)	72.6 (103.3)	79.5 (113.1)	70.9 (100.9)	101.7 (144.7)
% Elongation. Initial	343.3	251.9	193.6	408.9
Tear Strength. N/cm (lb/in)	46.1 (26.3)	36.4 (20.8)	54.5 (31.1)	59.5 (34.0)
After dry heat aging - 18 hrs. 104.4°C. % Elongation	264.0	186.4	176.5	389.6
Syneresis	None	None	None	None
Hydrolytic Stability - 7 days. 100°C, % Weight Change	--	+15.0	+4.8	+4.1

TABLE V

Components	16	17	18	19
Desmocup 11A	35.6	48.4	--	--
Vestanat IPDI	--	--	2.2	1.67
Arcol 34-28	--	27.7	--	--
Preparation A - 20% Epoxy resin dispersion in Poly L-385-29	49.4	--	--	--
Jeffamine T403	--	1.9	--	--
Preparation D - 35% Epoxy resin dispersion in Poly L-385-29	--	--	62.1	--
Castor Oil	--	--	18.7	--
Poly-L-385-29	--	--	--	30.67
Preparation E - 13% Epoxy resin dispersion in Castor Oil	--	--	--	56.66
Epon 826	10.0	20.0	15.0	--
BiCat 8	0.5	0.5	0.5	0.5
Irganox 1076	1.5	1.5	1.5	1.5
Expancel 551DU	3.0	--	--	--
3M Scotchlite GB S22	--	--	--	9.0
Cure	C	C	B	B
Isocyanate Index	100.1	65.7	26.7	9.5
Kerosene Immersion - 24 hrs. 38°C (100°F) - % Weight Change	--	+14.0	+9.7	+11.3
T <sub>g</sub> (from TMA) °C (°F)	--	-47.0 (-52.8)	-47.5 (-53.5)	-54.2 (-65.5)
Hardness, Shore 00	40.2	67.0	58.0	--
Hardness, 1/4 Cone	11.2	7.0	10.8	32.6
Density, gm/cc	--	--	--	0.664
Tensile Strength, N/cm <sup>2</sup> (psi)	--	38.0 (54.0)	71.3 (101.4)	5.6 (14.0)
% Elongation, Initial	--	186.0	295.1	638
Tear Strength, N/cm (lb/in)	--	21.0 (12.0)	--	6.7 (3.85)
After dry heat aging - 18 hrs. 104.4°C. % Elongation Syneresis	--	178.7 None	570.6 None	-- --
Hydrolytic Stability - 7 days. 100°C. % Weight Change	--	+4.2	--	--

Damping behavior as delineated by Tan delta was  
5 determined from a dynamic mechanical analysis performed

on a Rheometrics RDA-II (Rheometrics, Inc., Picataway, N.J.) at a 2 c/min. heating rate, nitrogen atmosphere, 7.9 min. disp. parallel plates at a test frequency of 1 Hz with an initial strain = 0.05%/Autostrain. The 5 temperature interval at Tan delta  $\geq$  0.6, the peak maximum of Tan delta and the temperature at which Tan delta is a maximum are shown in Table VI.

Table VI

Example	Tan delta amplitude (maximum)	Temp. Interval at Tan delta $\geq$ 0.6 ( $^{\circ}$ C)
8	1.21	-18 to -67 (maximum at -51.7)
19	2.07	+15 to -68 (maximum at -54.1)

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What is Claimed is:

1. A polypropylene ether polyol based polyurethane elastomer according to claim 1 comprising:

- 5 a) from 1 to 50 percent of at least one polyisocyanate component having the formula  $Q(NCO)_n$ , wherein n is an integer from 2 to 4, and Q is selected from the group consisting of an aliphatic hydrocarbon radical containing from 2 to 100 carbon atoms, and up to 50 heteroatoms; a cycloaliphatic  
10 hydrocarbon radical containing from 4 to 100 carbon atoms and zero to 50 heteroatoms; an aromatic hydrocarbon radical or heterocyclic aromatic radical containing from 6 to 15 carbon atoms and zero to 10 heteroatoms, and an araliphatic hydrocarbon radical  
15 containing from 8 to 100 carbon atoms and zero to 50 heteroatoms,
- b) from 20 percent to 94 percent of at least one isocyanate reactive component comprising at least one polypropylene ether polyol containing 15 to 40  
20 percent of a dispersion selected from polyadduct and polycondensate dispersions,
- c) from 5 to 35 percent of at least one epoxy compound, and
- d) from 0.1% to 5% of a catalyst for the reaction  
25 of said polyisocyanate component and said isocyanate reactive component;
- said elastomer having an isocyanate index of from 10 to 80, said elastomer exhibiting less than a 15% percent weight gain when a tensile dumbbell is immersed in  
30 kerosene for 24 hours at 38°C under ASTM D4(2).

2. A polypropylene ether polyol based polyurethane elastomer according to claim 1 wherein said epoxy is a

liquid epoxy compound having an epoxide equivalent weight of from 170 to 220.

3. A polypropylene ether polyol based polyurethane elastomer according to claim 1 wherein said epoxy is selected from the group consisting of reaction products of:

- a) polyphenols and epihalohydrins,
- b) polyalcohols and epihalohydrins,
- 10 c) polycarboxylic acids and epihalohydrins,
- d) amines and epihalohydrins,
- e) polyisocyanates and 2,3-epoxy-1-propanol, and
- f) mixtures of the above.

15 4. A polypropylene ether polyol based polyurethane elastomer according to claim 3 wherein said epoxy is selected from the group consisting of glycidyl ethers of bisphenol A compounds, brominated bisphenol A resins, phenolic resins, and mixtures thereof.

20

5. A polypropylene ether polyol based polyurethane elastomer according to claim 1 wherein said polyisocyanate is selected from the group consisting of 1-isocyanato-3,3,5-trimethyl-5-isocyanato-methyl  
25 cyclohexane (isophorone diisocyanate), dimer acid diisocyanate, 2,4'diphenyl methane diisocyanate and carbodiimide derivatives thereof, 4,4'diphenyl methane diisocyanate and carbodiimide derivatives thereof, 2,4'-tolylene diisocyanate, 2,6'- tolylene diisocyanate, and  
30 4,4'-methylene-bis(cyclohexyl diisocyanate).

6. A polypropylene ether polyol based polyurethane elastomer according to claim 1 wherein said polypropylene

ether polyol contains at least 65% oxypropylene units derived from propylene oxide, said polyol having a total unsaturation content of less than 0.08.

5        7. A polypropylene ether polyol based polyurethane elastomer according to claim 1 further comprising an additional polyol selected from the group consisting of polyether polyols based on ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, epichlorohydrin  
10 or mixtures thereof, ricinoleic acid derivatives, polyester polyols, polyamide or polyesteramide polyols; tertiary amine containing polyols, propoxylated amides or amines; polyalkadiene polyols derived from butadiene polymers or copolymers, and hydrogenated derivatives  
15 thereof; polyacetals, polycarbonates containing hydroxyl groups; polyhydroxyl (meth)acrylic resins, polythioether polyols, polyhydroxyl compounds already containing urethane or urea groups, and polymer polyols.

20        8. A polypropylene ether polyol based polyurethane elastomer according to claim 1 further comprising a polyamine selected from the group consisting of aminopolyethers, polyamidoamines, polyoxyalkylene polyamines, amine-terminated butadiene/acrylonitrile  
25 copolymers, aminoalkyl terminated polydiorganosiloxanes, polytetramethylene oxide-di-aminobenzoates, polyethers containing aromatic amine end groups and amine-terminated polyethers containing a moiety selected from urea, amide, ester and urethane moieties in the polymer backbone.

30

9. A polypropylene ether polyol based polyurethane elastomer according to claim 1 comprising from 10 percent to 60 percent of at least one plasticizer selected from

the group consisting of polyalphaolefins, cyclic polyolefins, petroleum oils, vegetable oils, naphthenic oils, paraffinic oils, synthetic oils, phosphate esters, monoesters, diesters, polyesters, rosin esters, pine oil, 5 coal tar, glyceryl-tri(acetylricinoleate) and mixtures thereof.

10. A polypropylene ether polyol based polyurethane elastomer according to claim 12 wherein said reaction 10 product has an isocyanate index of less than 65.

11. A polypropylene ether polyol based polyurethane elastomer according to claim 1 further comprising from 10 to 60 volume percent hollow microspheres selected from 15 the group consisting of glass microspheres, expanded and unexpanded polymeric microspheres, and ceramic microspheres.

12. A sealant for a signal conducting device 20 comprising a polypropylene ether polyol based polyurethane elastomer according to claim 1.

13. A signal transmission component wherein said device comprises 25 a) an outer closure member capable of enclosing a cable splice, said cable splice having at least one set of wires penetrating said splice, and b) a means for sealing said outer closure comprising an endseal composed of a polypropylene 30 ether polyol based polyurethane elastomer according to claim 1, said endseal being positioned between said outer closure and said at least one set of

wires, said endseal having means formed therein for passage of said wires.

14. A signal transmission component according to  
5 claim 13 wherein said device comprises

- a) an outer closure capable of enclosing a cable splice and
- b) a resealable sealing means composed of a polypropylene ether polyol based polyurethane elastomer according to claim 1, and  
10
- c) a means for compression, said sealing means being maintained under compression.

# INTERNATIONAL SEARCH REPORT

Inter. nal Application No

PCT/US 95/06162

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L75/04 C08G18/40 C08G18/63 H01B3/30 C08J9/32  
C09K3/10 //(C08L75/04,63:00)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C08L C09D C09K H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,30 01 637 (MICAFIL AG) 23 July 1981 see claims 1-4 see page 7, paragraph 1 -paragraph 2 ---	1
A	EP,A,0 232 124 (DOW) 12 August 1987 see claims 1-5 & US,A,4 789 690 cited in the application ---	1
A	WO,A,94 00504 (MINNESOTA MINING) 6 January 1994 see claims 1,8-15 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

24 August 1995

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/06162

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WO-A-9400504	06-01-94	CA-A- 2137453 EP-A- 0648237	06-01-94 19-04-95

